

- B. pressurizing a gas phase polymerization reactor with the at least one  $\alpha$ -olefin monomer to be polymerized;
- C. introducing the recovered supported catalyst to the gas phase polymerization reactor;
- D. activating the recovered supported catalyst; and
- E. recovering polymerized product from the reactor.

*A3  
Amended*

20. (Amended) The process of Claim 19, further comprising providing to the reactor a tri(hydrocarbyl)aluminum compound having from 1 to 10 carbons in each hydrocarbyl group, an oligomeric or polymeric alumoxane compound, a di(hydrocarbyl)(hydrocarbyloxy)aluminum compound having from 1 to 10 carbons in each hydrocarbyl or hydrocarbyloxy group, or a mixture of the foregoing compounds, wherein such providing occurs either prior to, during, or subsequent to the introduction to the reactor of the recovered supported catalyst.

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#### **REMARKS**

Enclosed is an abstract on a separate sheet of paper in compliance with M.P.E.P. § 608.01(b).

Claims 1, 5-9, and 18-20 have been amended to avoid the Examiner's objections to the claims and for clarity. Support for the definition of R can be found on page 25, line 6 in combination with page 26, lines 2-4. Support for the complex being of a metal of Group 3, 4, or the Lanthanide metals can be found on page 5, line 28. No amendments have been made in view of the cited prior art. Withdrawal of the noted objections to the claims is requested.

In the Office Action, the Examiner rejected claims 1-3, 5-9, 15, and 17-20 under 35 U.S.C. § 103(a) for being obvious over U.S. Patent No. 5,227,440 to Canich et al. (Canich). In addition, claims 1-20 were rejected for being obvious over U.S. Patent No. 6,025,448 to Swindoll et al. (Swindoll) in view of Canich, claims 1-13 and 15-19 for being obvious over WO 98/45337 to Peil et al. (Peil), claim 14 over Peil in view of Swindoll, and claim 20 over Peil in view of Canich.

The present invention relates to a process for preparing an olefin polymerization catalyst and a process for polymerizing at least one  $\alpha$ -olefin monomer using the catalyst in which first and second solutions are applied to a support, the first solution in a compatible solvent being one of a complex of a metal of Group 3, 4 or the Lanthanide metals or of a selected cocatalyst, and the second solution in a compatible solvent being the other of the complex or the cocatalyst, wherein the second solution (and optionally additionally the first) is applied in an amount that does not exceed the pore volume of the support. See amended claim 1, lines 25 to 27 and amended claim 19, lines 29 to 31.

Procedures for preparing the supported catalysts of the present invention are described in detail on pages 27-29 of the specification. The procedures include either a sequential double impregnation whereby in each of the two contacting steps, the contacting solution is provided in an amount such that 100% of the pore volume of the support is at no time exceeded. In this way, a free-flowing powder is obtained after the contact with the first solution. Alternatively, after contact between the support and the first solution, sufficient solvent is removed to provide a free-flowing supported

procatalyst, which is then contacted with the second solution which is present in an amount less than 100% of the pore volume of the support.

Examples 2, 4, and 5 (pages 36 and 37) illustrate the double impregnation method, while Example 1 (page 36) illustrates the method whereby after the first contact, sufficient solvent is removed until the fluidization of the powder ceased.

Comparative Example 3 (page 36) illustrates a procedure where after the addition of the first solution, the solvent is not removed (and hence no free-flowing powder is obtained) and the resultant slurry is then treated with the second solution. In this Example, there is clearly excess solvent present, i.e., greater than the pore volume of the support.

The advantages of the present invention are well documented at pages 27-29 of the specification. In particular, it is an advantage that the catalyst and cocatalyst are not mixed prior to contact with the support, thereby providing improved stability. Also, the amount of solvent used is minimized aiding catalyst deactivation.

With cocatalysts which are heat sensitive, advantages occur due to the reduced heating needed to remove the excess solvents used in prior art preparations.

The noted Examples clearly illustrate the unobviousness of the present invention. In particular, the supported catalyst of Comparative Example 3 prepared by the slurring procedure exhibited an exotherm of 30°C on introduction into the reactor followed by a steeply decaying kinetic profile. In contrast, Example 1 of the invention exhibited an exotherm of 16°C followed by a gently decaying kinetic profile. In the more preferred Examples 2, 4, and 5, exotherms of 5.5°C, 7.9°C, and 5°C respectively were observed with either moderately decaying or stable kinetic profiles.

Although the pore volume of the supports used in Canich are similar to those used in the present invention and the support is also pretreated with, for example, an alkylaluminium compound, the key is the amount of solvent used in the preparation of the supported catalysts.

Canich generally discloses that the contact between the support, catalyst, and cocatalyst may take place in any order, including where the latter components are premixed before contact with the support.

However, neither the specification nor any of the Examples in Canich teach the present invention. As noted above, an advantage of the present invention is the avoidance of having to mix the catalyst and cocatalyst together prior to contact with the support. In the majority of the Examples in Canich, the metallocene and the alminoxane are combined together before contact with the support.

In Example 2 of Canich, the catalyst and cocatalyst are sequentially added to the support. However, there is neither removal of the solvent or a free-flowing powder obtained after the addition of the first solution and the preparation is clearly performed in the slurry phase, indicating an excess of solvent whereby the pore volume would be expected to be exceeded.

In Example 8 of Canich, which does not combine the components before contact, there is subsequent addition of the catalyst, but not the cocatalyst. In this Example, the cocatalyst (aluminoxane) is prepared directly on the support by reaction of water and an alkyl aluminium compound.

In addition, all the Examples of Canich illustrate the use of an aluminoxane. In the present invention, the cocatalysts are non-polymeric, non-oligomeric complexes and

these are described on pages 16-22 of the specification. Aluminoxanes are oligomeric or polymeric aluminium oxy-compounds and hence are different from the cocatalysts of the present invention.

None of the Examples in Canich therefore describe the preparation of the supported catalysts of the present invention. There is no teaching in Canich of the need to maintain the amount of solvent below the pore volume of the support. The fact, as the Examiner notes, that since the pore volumes of the support material and the loading are similar to those in the present invention does not lead to any assumptions regarding the amount of solvent to be used in the preparation.

In view of the lack of any teaching in Canich about not exceeding the pore volume of the support when the second solution of the metal complex or cocatalyst in a compatible solvent is applied to the support and because of the unexpected advantages resulting from this procedure in the process of preparing the polymerization catalyst as demonstrated by the Examples, it is not seen how the claimed invention can be considered obvious over Canich. Its withdrawal as a ground of rejection of the claims is therefore requested.

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With respect to Swindoll, the Examiner again makes similar assumptions as made for Canich – pore volume, nature of the metallocene, as well as the disclosure of a number of different permutations for the catalyst preparation. The Examiner then makes the assumption that because several methods of preparation are disclosed, one of them must inherently cover the process where 100% of the pore volume of the support is not exceeded, inviting applicants to establish otherwise.

It is submitted that by comparing Examples 1, 2, 4, and 5 with Example 3, that applicants have established that it cannot be said that the prior art processes of Swindoll inherently include applicants' process or that Swindoll suggests in any way to the man skilled in the art to conduct the process according to applicants' claims.

In Swindoll, Examples 9-19 (and also 20-25) describe the preparation of the supported catalysts based on silica. The same general preparation is used whereby solutions of both the catalyst and the cocatalyst are added to the silica. Even if these were sequential, then there is no teaching of removing the solvent or forming a free-flowing powder. These Examples, as in Example 2 of Canich, teach the use of a slurry to prepare the supported catalysts, indicating an excess of solvent whereby the pore volume would be expected to be exceeded.

Withdrawal of the rejection based on Swindoll in view of Canich is therefore also requested.

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Peil also discloses a process for the preparation of a supported catalyst comprising slurrying the support with solutions of the catalyst and the cocatalyst. As discussed above, such slurrying processes, by definition, involve amounts of liquid in excess of the pore volume of the support. For example, compare the liquid/support ratios during addition of the catalyst and the cocatalyst of Peil with those of the present invention. In particular, while the Examples of the present invention use an order of 1.25 mL (or less) of hydrocarbon diluent per gram of support in the second solution, Peil uses an amount from about 5 to over 1000 mL of hydrocarbon diluent per gram of support. Clearly this indicates an excess of solvent whereby the pore volume would be expected to be exceeded.

In any event, just as in Canich or Swindoll, Peil fails to teach the claimed limitation of providing the second solution "in an amount such that 100% of the pore volume of the support precursor is not exceeded" in a process for preparing a polymerization catalyst and it cannot be considered obvious from of what is taught in Peil in view of the unexpected and superior results achieved by applicants' process.

Withdrawal of the rejection of the claims for being obvious over Peil is therefore requested.

Swindoll and Canich may disclose what they are being cited for when combined with Peil, but the fact remains that they, as discussed above, fail to disclose what is missing in Peil. Accordingly, withdrawal of the rejection based on Peil in view of Swindoll and Peil in view of Canich is therefore also requested.

It is believed claims 1-20 are in condition for allowance and said action is therefore requested.

Please grant any extensions of time required to enter this Amendment and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

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Dated: June 23, 2003

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## APPENDIX TO AMENDMENT OF JUNE 23, 2003

### Version with Markings to Show Changes Made

#### Amendments to the Claims

1. (Amended) A process for preparing an olefin polymerization catalyst comprising the steps of:

- A. calcining silica at a temperature of 30 to 1000°C to form calcined silica,
- B. reacting the calcined silica with an agent selected from the group consisting of:
  - i. Lewis acid alkylating agents,
  - ii. silane or chlorosilane functionalizing agents, and
  - iii. aluminum components selected from an alumoxane or an aluminum compound of the formula  $[AlR^1_xR^2_{y'}] AlR^1_xR^2_{y'}$ , wherein  $R^1$  independently each occurrence is hydride or R,  $R^2$  is hydride, R or OR, wherein R is a C<sub>1</sub> to C<sub>10</sub> hydrocarbyl group,  $x'$  is 2 or 3,  $y'$  is 0 or 1 and the sum of  $x'$  and  $y'$  is 3,to form a support precursor having a specified pore volume,
- C. applying to the support precursor a first solution in a compatible solvent of one of the following:
  - (1) a complex of a metal of [Groups 3-10] Group 3, 4, or the Lanthanide metals of the Periodic Table of the Elements or
  - (2) a cocatalyst selected from the group consisting of non-polymeric,



non-oligomeric complexes capable of activating the complex of [(C)(i)] (C)(1) for the polymerization of  $\alpha$ -olefins and optionally removing the compatible solvent of the first solution to form a supported procatalyst;

- D. applying to the supported procatalyst a second solution in a compatible solvent of the other of the [catalyst] complex or the cocatalyst of (C) to form a supported catalyst, wherein the second solution is provided in an amount such that 100 percent of the pore volume of the support precursor is not exceeded; and
- E. optionally removing the compatible solvent of the second solution from the supported catalyst to form a recovered supported olefin polymerization catalyst [system].

5. (Amended) The process of Claim 1, wherein the [Group 3-10 metal] complex is  $L_1MX_mX'_nX''_p$ , or a dimer thereof wherein:

L is an anionic, delocalized,  $\pi$ -bonded group that is bound to M, containing up to 50 [nonhydrogen] non-hydrogen atoms, optionally two L groups may be joined together through one or more substituents thereby forming a bridged structure, and further optionally one L may be bound to X through one or more substituents of L;

M is a metal of Group 4 of the Periodic Table of the Elements in the +2, +3 or +4 formal oxidation state;

X is an optional, divalent substituent of up to 50 non-hydrogen atoms that together with L forms a metallocycle with M;

X' is an optional neutral Lewis base having up to 20 non-hydrogen atoms;

X" each occurrence is a monovalent, anionic moiety having up to 40 non-hydrogen atoms, optionally, two X" groups may be covalently bound together forming a divalent dianionic moiety having both valences bound to M, or form a neutral, conjugated or nonconjugated diene that is  $\pi$ -bonded to M (whereupon M is in the +2 oxidation state), or further optionally one or more X" and one or more X' groups may be bonded together thereby forming a moiety that is both covalently bound to M and coordinated thereto by means of Lewis base functionality;

l is 1 or 2;

m is 0 or 1;

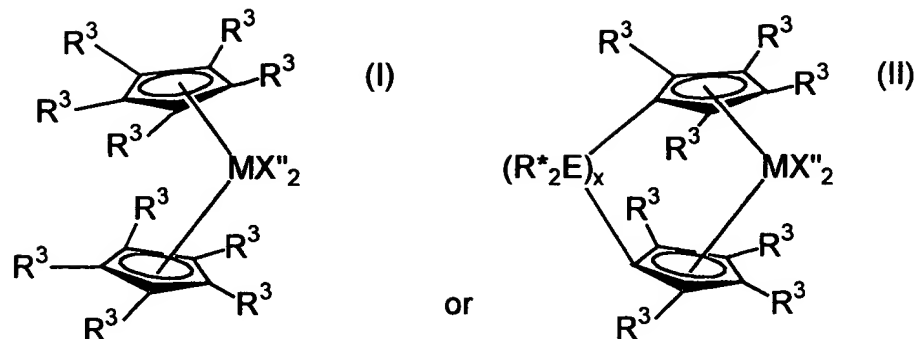
n is a number from 0 to 3;

p is an integer from 0 to 3; and

the sum,  $l+m+p$ , is equal to the formal oxidation state of M.

6. (Amended) The process of Claim 5, wherein the [Group 3 - 10 metal] complex contains two L groups which are linked by a bridging group, wherein the bridging group corresponds to the formula  $(ER^*_2)_x$ , wherein E is silicon or carbon,  $R^*$  independently each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, said  $R^*$  having up to 30 carbon or silicon atoms, and x is 1 to 8.

7. (Amended) The process of Claim 5, wherein the [Group 3 - 10 metal] complex corresponds to the formula:



wherein:

M is titanium, zirconium or hafnium, [preferably zirconium or hafnium,] in the +2 or +4 formal oxidation state;

$R^3$  in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, [said  $R^3$  having up to 20 non-hydrogen atoms,] or adjacent  $R^3$  groups together form [a divalent derivative (that is,) a hydrocarbadiyl, siladiyl or germadiyl group[]] thereby forming a fused ring system, [and]

$X''$  independently each occurrence is an anionic ligand group of up to 40 [nonhydrogen] non-hydrogen atoms, or two  $X''$  groups together form a divalent anionic ligand group of up to 40 [nonhydrogen] non-hydrogen atoms or together are a conjugated diene having from 4 to 30 non-hydrogen atoms forming a  $\pi$ -complex with M, whereupon M is in the +2 formal oxidation state, [and

$R^*$ , E and x are as previously defined.]

E is silicon or carbon,

$R^*$  independently each occurrence is hydrogen or a group selected from silyl,

hydrocarbyl, hydrocarbyloxy and combinations thereof, said R\* having up to 30 carbon or silicon atoms, and

x is 1 to 8.

8. (Amended) The process of Claim 1, wherein the [Group 3 - 10 metal] complex corresponds to the formula:



wherein:

L is an anionic, delocalized,  $\pi$ -bonded group that is bound to M, containing up to 50 [nonhydrogen] non-hydrogen atoms;

M is a metal of Group 4 of the Periodic Table of the Elements in the +2, +3 or +4 formal oxidation state;

X is a divalent substituent of up to 50 non-hydrogen atoms that together with L forms a metallocycle with M;

X' is an optional neutral Lewis base ligand having up to 20 non-hydrogen atoms;

X'' each occurrence is a monovalent, anionic moiety having up to 20 non-hydrogen atoms, optionally two X'' groups together may form a divalent anionic moiety having both valences bound to M or a neutral C<sub>5-30</sub> conjugated diene, and further optionally X' and X'' may be bonded together thereby forming a moiety that is both covalently bound to M and coordinated thereto by means of Lewis base functionality;

l is 1 or 2;

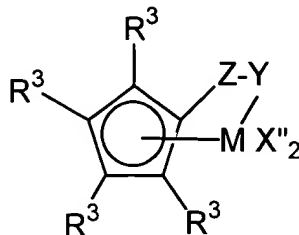
m is 1;

n is a number from 0 to 3;

p is an integer from 1 to 2; and

the sum,  $l+m+p$ , is equal to the formal oxidation state of M.

9. (Amended) The process of Claim 8, wherein the [metal] complex corresponds to the formula:



wherein:

M is titanium or zirconium in the +2 or +4 formal oxidation state;

R<sup>3</sup> in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, [said R<sup>3</sup> having up to 20 non-hydrogen atoms,] or adjacent R<sup>3</sup> groups together form [a divalent derivative (that is,) a hydrocarbadiyl, siladiyl or germadiyl group[]] thereby forming a fused ring system,

each X'' is a halo, hydrocarbyl, hydrocarbyloxy or silyl group, said group having up to 20 [nonhydrogen] non-hydrogen atoms, or two X'' groups together form a C<sub>5-30</sub> conjugated diene;

Y is -O-, -S-, -NR\*, -PR\*-, and

Z is SiR\*<sub>2</sub>, CR\*<sub>2</sub>, SiR\*<sub>2</sub>SiR\*<sub>2</sub>, CR\*<sub>2</sub>CR\*<sub>2</sub>, CR\*=CR\*, CR\*<sub>2</sub>SiR\*<sub>2</sub>, or GeR\*<sub>2</sub>,

wherein: R\* [is as previously defined] independently each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, said

18. (Amended) The process of Claim 1, wherein at least one of the supported procatalyst or the supported catalyst is treated by at least one of the following:

- a. applying thereto a vacuum of from 0.05 to 150 Torr; or
- b. heating to a temperature of [from 0] up to 60°C.

19. (Amended) A process for polymerizing at least one  $\alpha$ -olefin monomer comprising:

A. preparing a supported [cocatalyst] catalyst by:

- i. calcining silica at a temperature of 30 to 1000°C to form calcined silica,
- ii. reacting the calcined silica with an agent selected from the group consisting of:
  - (a) Lewis acid alkylating agents,
  - (b) silane or chlorosilane functionalizing agents, and
  - (c) aluminum components selected from an alumoxane or an aluminum compound of the formula  $[AlR^1_xR^2_y] \underline{AlR^1_xR^2_y}$ , wherein  $R^1$  independently each occurrence is hydride or R,  $R^2$  is hydride, R or OR, wherein R is a  $C_1$  to  $C_{10}$  hydrocarbyl group,  $x'$  is 2 or 3,  $y'$  is 0 or 1 and the sum of  $x'$  and  $y'$  is 3,to form a support precursor having a specified pore volume,
- iii. applying to the support precursor a first solution in a

- iii. applying to the support precursor a first solution in a compatible solvent of one of the following:
  - (a) a complex of a metal of [Groups 3-10] Group 3, 4, or the Lanthanide metals of the Periodic Table of the Elements or
  - (b) a cocatalyst selected from the group consisting of non-polymeric, non-oligomeric complexes capable of activating the complex of [(C)(i)] (iii)(a) for the polymerization of  $\alpha$ -olefinsand optionally removing the compatible solvent of the first solution to form a supported procatalyst;
- iv. applying to the recovered supported procatalyst a second solution in a compatible solvent of the other of the [catalyst] complex or cocatalyst of [(C)] (iii) to form a supported catalyst, wherein the second solution is provided in an amount such that 100 percent of the pore volume of the support precursor is not exceeded; and
- v. optionally removing the compatible solvent of the second solution from the supported catalyst to form a recovered supported catalyst [system];
- B. pressurizing a gas phase polymerization reactor with the at least one  $\alpha$ -olefin monomer to be polymerized;
- C. introducing the recovered supported catalyst [system] to the gas

- D. activating the recovered supported catalyst [system]; and
- E. recovering [the] polymerized product from the reactor.

20. (Amended) The process of Claim 19, further comprising providing to the reactor a tri(hydrocarbyl)aluminum compound having from 1 to 10 carbons in each hydrocarbyl group, an oligomeric or polymeric alumoxane compound, a di(hydrocarbyl)(hydrocarbyloxy)aluminum compound having from 1 to 10 carbons in each hydrocarbyl or hydrocarbyloxy group, or a mixture of the foregoing compounds, wherein such providing occurs either prior to, during, or subsequent to the introduction to the reactor of the recovered supported catalyst [system].



## ABSTRACT

A process for preparing an olefin polymerization catalyst and a process for polymerizing one or more  $\alpha$ -olefins in the presence of the olefin polymerization catalyst wherein a calcined and passivated silica support (support precursor) is sequentially contacted with a first solution of a metal complex or of a cocatalyst, and thereafter with a second solution of the other of the metal complex or the cocatalyst, wherein the second solution is provided in an amount such that 100 percent of the pore volume of the support precursor is not exceeded. Optionally, the compatible solvent of the first and/or second solutions is removed.